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FINAL REPORT

"Epitaxial III-V Semiconductors for Integrated Electro-optics"

Contract No. N00014-86-K-0622

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Research has been conducted on the synthesis and evaluation of new organometallics (OM), growth of epitaxial layers by OMCVD and laser chemical vapor deposition (LCVD), laser interaction with materials, structural and chemical evaluation of epitaxial layers, electrical evaluation of epitaxial layers and radiation effects in semiconductors and insulators. New OM precursors were developed and used in OMCVD. New OM sources are considered for lower toxicity and more efficient reaction. For the first time, InSb was grown in CdTe by OMCVD. A quadrupole mass analyzer and low temperature luminescence were installed for in situ diagnostics. Laser interaction studies reveal the importance of tunneling ionization for carrier generation in low bandgap materials. Ion emission has been measured from a metal surface due to laser irradiation. Ions were observed at low laser fluence and at a frequency corresponding to an energy less than the material work function. Rocking curve studies of MBE-grown strained GaInAs on GaAs is the most

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most reliable technique for strains <0.3%. LO-TO splitting in ion-damaged GaAs has been explained by the effective ionic charge of the ion beam-induced point defects. Deep level transient spectroscopy studies of irradiated p-InP has revealed trap levels and annealing effects of importance in extraterrestrial applications. A Yb/p-InP device has shown good linearity and improved stability as a temperature sensor from 100-400°K. Thin (150 Å) oxides on Si for VLSI applications were found to be more radiation tolerant compared to thicker oxides.

A major planned activity of this project involved the expansion of research facilities in the area of electronic materials. This expansion was aided by the University establishment of a Center for Electronic and Electro-optic Materials (CEEM). The following capabilities have been added in the past 2-3 years:

1) Two clean rooms for device processing.

2) III-V epitaxial growth by liquid phase epitaxy and organometallic chemical vapor deposition.

3) Laser chemical vapor deposition.

4) 10K - 400K automated current-voltage test station.

5) 77K - 400K deep level transient spectroscopy and quasistatic C-V.

6) Low temperature Hall effect.

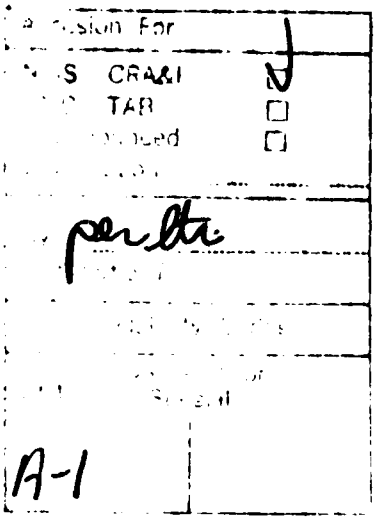
7) Double crystal x-ray rocking curve and topography.

8) Reflectance spectroscopy.

9) High pressure diamond anvil experiment.

10) Fine line lithographic capability.

Five faculty have been added in the area of electronic materials. Three faculty on the ONR project have received NSF-PYI awards (H.K., P.L., C.W.). The Center for Electronic and Electro-optic Materials now has 13 faculty having a focus principally on III-V semiconductors with a small effort in the polymer area.



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ABSTRACT

Research has been conducted on the synthesis and evaluation of new organometallics (OM), growth of epitaxial layers by OMCVD and laser chemical vapor deposition (LCVD), laser interaction with materials, structural and chemical evaluation of epitaxial layers, electrical evaluation of epitaxial layers and radiation effects in semiconductors and insulators. New OM precursors were developed and used in OMCVD. New OM sources are considered for lower toxicity and more efficient reaction. For the first time, InSb was grown in CdTe by OMCVD. A quadrupole mass analyzer and low temperature luminescence were installed for in situ diagnostics. Laser interaction studies reveal the importance of tunneling ionization for carrier generation in low bandgap materials. Ion emission has been measured from a metal surface due to laser irradiation. Ions were observed at low laser fluence and at a frequency corresponding to an energy less than the material work function. Rocking curve studies of MBE-grown strained GaInAs on GaAs is the most reliable technique for strains <0.3%. LO-TO splitting in ion-damaged GaAs has been explained by the effective ionic charge of the ion beam-induced point defects. Deep level transient spectroscopy studies of irradiated p-InP has revealed trap levels and annealing effects of importance in extraterrestrial applications. A Yb/p-InP device has shown good linearity and improved stability as a temperature sensor from 100-400°K. Thin (150 Å) oxides on Si for VLSI applications were found to be more radiation tolerant compared to thicker oxides.

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TASK 1

Synthesis of Organometallic Precursors for OMCVD

O.T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo

Ella F. Spiegel, M.A. awarded 1987

John D. Maloney, Ph.D. expected in 1990

Technical Summary

The emphasis of our research has been on the synthesis and characterization of organoderivatives of gallium and indium. The initial research centered on the neopentyl derivatives of indium, $In(CH_2CMe_3)_3$, $In(CH_2CMe_3)_2Cl$, $In(CH_2CMe_3)Cl_2$ and $In(CH_2CMe_3)_2Me$. These compounds were characterized by elemental analyses, cryoscopic molecular weight studies, ^1H NMR and IR spectroscopic studies and Lewis acidity studies, as appropriate. The neopentyl group was selected as the organic substitutent because of its large steric size, its electron withdrawing properties and its potential for reaction chemistry. The large size of the neopentyl groups and its lack of β-hydrogen atoms make $In(CH_2CMe_3)_3$ very easy to prepare by a typical Grignard reaction in diethylether solution. Ether adducts are unstable at room temperature. Thus, the parent compound can be isolated easily by sublimation, at 50-100°C. The compound has 2 mm of vapor pressure at 55°C. The second feature of the neopentyl group which makes it so attractive for OMCVD reactions is its potential for thermal decomposition at <u>high</u> temperatrues to form methyl-metal derivatives and 2-methylpropene. This type of decomposition pathway which has been observed

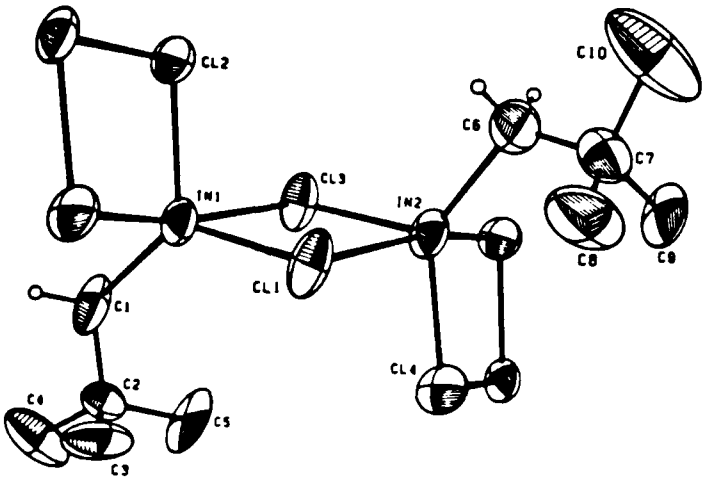
$$In(CH_2CMe_3)_3 \longrightarrow InMe_3 + 3\ CH_2 = CMe_2$$

in a mass spectrometer suggests that $In(CH_2CMe_3)_3$ and its derivatives should react like the methyl derivatives at the higher temperatures (> 300°C) used for

OMCVD. Experimental results of Professor Liu involving the preparation of InSb from $In(CH_2CMe_3)_3$ and $SbMe_3$ have verified our hypothesis. We are anxious to learn the results of his experiments to prepare InP from $In(CH_2CMe_3)_3$ and PH_3.

The new compound $In(CH_2CMe_3)_2Me$ is an attractive alternative to $In(CH_2CMe_3)_3$. This monomethyl derivative is a volatile, nonpyrophoric liquid at room temperature. In contrast, $In(CH_2CMe_3)_3$ is a less volatile, nonpyrophoric solid with a melting point of 55-57°C. The preparative route to $In(CH_2CMe_3)_2Me$ involved the initial synthesis of $In(CH_2CMe_3)_3$, conversion to $In(CH_2CMe_3)_2Cl$ in a quantitative ligand redistribution reaction with $InCl_3$ and alkylation by LiMe in ether. The product was readily isolated by distillation.

The dicholoroderivative $In(CH_2CMe_3)Cl_2$ is very interesting as it exists as a "ladder polymer" with five coordinate indium. This compounds unusual chemical features, unexpectedly high melting point (>200°C) and insolubility in common organic solvents, suggested some type of unusual structure in the solid state. Professor Robin Rogers of Northern Illinois University collected the diffraction data and solved the structure for us. The following diagram gives the repeating unit of this polymer. The structure of $In(CH_2CMe_3)_2Cl$ will also be investigated.



The phosphides $(Me_3CCH_2)_2InPPH_2$ and $(Me_3CCH_2)(Cl)InPPh_2$ have been prepared and characterized. The derivative $(Me_3CCH_2)_2InPPh_2$, which is prepared from $In(CH_2CMe_3)_3$ and PPh_2H in refluxing pentane, is most interesting. The compound exists as a monomer-dimer equilibrium mixture in benzene solution, but a structural study by Professor Melvyn R. Churchill and his student James C. Fellinger revealed a trimer in the solid state. These observations confirm that thermodynamic factors, not kinetic, control the degree of association of 3-5 compounds. The stronger the bonding for association, the higher the temperature needed for remaining elimination reactions. The compound $(Me_3CCH_2)(Cl)InPPh_2$ exists as a trimer in benzene solution. Thus, the replacement of a neopentyl group by chlorine serves to strengthen indium phosphorus bonds in associated species. The purpose of preparing $[(CMe_3CCH_2)(Cl)InPPh_2]_3$ was to use it for the preparation of $(Me_3CCH_2)(Me)InPPh_2$. The compound $(Me_3CCH_2)(Me)InPPh_2$ might be alternatively prepared from $In(CH_2CMe_3)_2Me$ and PPh_2H by an elimination reaction. Experimental results must be used to determine whether CMe_4 or CH_4 is formed. This last experiment remains to be completed.

Publications

1. O.T. Beachley, Jr., U.S. Patent 4,710,575 (December 1, 1987), "Bisneopentyl Alkyl Organometallic Compounds and Methods of Preparing".
2. The results of the research will be published in American Chemical Society Journals in the near future.

Conference

1. John D. Maloney, Michael A. Banks and O.T. Beachley, Jr., "Syntheses, Characterizations and Comparisons of Organo-group 13 Diphenylphosphides" Third Chemical Confree of North America, Toronto, Canada, June 8, 1988.
2. J.C. Chen, W.K. Chen, P.L. Liu, J. Maloney and O.T. Beachley, Jr., "Metalorganic Chemical Vapor Deposition of InSb Using Trineopentylindium". SPIE Meeting January 1988, Los Angeles, CA.

TASK 2

Metalorganic Chemical Vapor Deposition of Compound Semiconductors

Pao-Lo Liu
Department of Electrical and Computer Engineering
State University of New York at Buffalo

W.-K. Chen
Ph. D. expected in January 1989

J.-C. Chen
Ph. D. expected in January 1989

Abstract

In this project, we have demonstrated the use of tri-neopentyl indium for depositing InSb films. We have also developed a precracking technique and deposited InSb on CdTe.

Technical Summary

Metalorganic chemical vapor deposition (MOCVD) has been used to deposit various high quality films for electronic and optoelectronic applications. Since MOCVD can be easily scaled up, it has been identified as the major candidate for industrial production of compound semiconductors. Nevertheless, because of the toxicity of many precursors, very limited work has been done especially among universities. We took the initiative to install and operate an MOCVD system. Our interests include evaluation of new precursors, deposition of III-V on II-VI, and atomic layer epitaxy, i. e., the growth of very thin layers of controllable compositions by MOCVD.

During the last one and half years, we have demonstrated the growth of InSb on InSb using the recently synthesized tri-neopentyl indium ($InNp_3$) as the precursor for indium. We have also succeeded in depositing InSb films on CdTe. The inter-diffusion problem is solved by using a pre-cracking stage,

therefore, the substrate is always maintained at a reduced temperature. The films grown have been characterized by optical microscopy, scanning electron microscopy, and x-ray diffraction.

1. Growth of InSb Using Tri-Neopentyl Indium

For epitaxial growth of indium compounds, typically, one uses tri-methyl indium (TMIn) or tri-ethyl indium (TEIn).[1,2] These materials are relatively expensive to synthesize and are quite pyrophoric. To replace them, a new compound, $InNp_3$ has been synthesized by Prof. O. T. Beachley, Jr. on our campus. $InNp_3$ is easy to synthesize and to purify. It is a solid at room temperature. It is non-pyrophoric. It has an adequate volatility, e. g., 2 torr @ 55 ^{o}C. Such properties make $InNp_3$ rather ideal for MOCVD.

We incorporated the $InNp_3$ into our atmospheric pressure MOCVD system. InSb substrates with (100), (110), and (111)-B orientations were used. The right growth conditions were found experimentally. We held the $InNp_3$ bubbler at 55 ^{o}C. Tri-methyl antimony (TMSb) was used as the Sb source. TMSb was maintained at 0 ^{o}C. Pd-diffused H_2 was used as the carrier gas at a flow rate of 1000 cm^3/min. The partial pressure ratio of group III to group V source was maintained at 0.5 by flow rate controllers. The substrate was maintained at 450 ^{o}C on a graphite substrate holder.

The quality of epitaxial layers grown were analyzed by a scanning electron microscope (SEM) and by x-ray diffraction. According to the SEM analysis, the films are stoichiometric. There are hillocks formed on the (111)-B substrate [3]. The (111) x-ray diffraction peak has a full

width at half maximum (FWHM) of 105 arc sec. In comparison, the substrate has a FWHM of 93 arc sec. Layers grown using TMIn have a FWHM of 70 arc sec.

We conclude that $InNp_3$ can be used as a new precursor for growing Indium compounds epitaxially.

2. Low Temperature Hetero-Epitaxy of InSb on CdTe

InSb has a very high electron mobility. CdTe-HgCdTe is a very important material system for infrared detection. It turns out that InSb is nearly lattice matched to CdTe-HgCdTe. At room temperature, the relative lattice mismatch is only 0.05%. By combining a II-VI compound, which has a widely adjustable bandgap, with III-V, which has a high electron mobility, new applications can be developed.

One major problem in growing the InSb/CdTe system is inter-diffusion. When the substrate temperature is higher than 305 ^{o}C, CdTe easily inter-diffuses into the epilayer. The composition becomes uncontrollable.[4] On the other hand, in order to crack precursors in the MOCVD system, the substrate must be maintained at least at 400 ^{o}C. We have developed a simple, yet very effective approach to avoid inter-diffusion. By using a precracking stage in front of the substrate, we are able to grow InSb without inter-diffusion at temperature as low as 185 ^{o}C. Our work represents the first successful growth of InSb on CdTe using a MOCVD system.

A molybdenum platform maintained at 425 ^{o}C was used as the precracking stage. The CdTe substrate was placed on a graphite substrate holder. The temperature of the substrate holder was controlled by an

accurate temperature controller. The lowest temperature was limited by thermal diffusion from the precracking stage to 185 °C. The growth rate is independent of the temperature of the substrate holder. It clearly indicates that the precracking stage effectively cracks all precursors.

The films grown were analyzed by SEM. Based on energy dispersive x-ray analysis, we conclude that the InSb film is stoichiometric. However, films grown above 400 °C, are clearly not stoichiometric. An InTe compound becomes the dominant composition. Films grown at 240 °C were characterized by x-ray diffraction. We can resolve distinct diffractions peaks of the substrate and the epilayer. Since the relative lattice mismatch is only 0.05% at room temperature, the quality of the epilayer is clearly very good.

In conclusion, we have developed a precracking technique in deposition InSb on CdTe. High crystallinity InSb epilayers have been obtained.

3. New Progress

Recently, we have installed a quadrupole mass analyzer (QMA) and a low temperature luminescence setup. With the QMA, we can find the mechanism as well as the efficiency of new precursors. A pressure balancing network has also been incorporated into the MOCVD system. We are currently growing InP. Preliminary data indicate that we can grow layers as thin as 20 Å.

References:

1. P. K. Chiang and S. M. Bedair, J. Electrochem. Soc., **131**, 2422 (1984).
2. O. Sugiura and M. Matsumura, Jap. J. Appl. Phys., **24**, L925 (1985).
3. T. Ohashi, Ph. D. thesis, Cornell University, (1986).
4. K. Sugiyama, J. Cryst. Growth, **60**, 450 (1982).

Journal Publications:

1. J. C. Chen, W. K. Chen, and Pao-Lo Liu, "Metalorganic Chemical Vapor Deposition of InSb Using Tri-Neopentyl Indium," SPIE Proceed. vol. 877, in print.

2. J. C. Chen, P. Bush, W. K. Chen, and Pao-Lo Liu, "Low Temperature Heteroepitaxial Growth of InSb on CdTe by Metalorganic Chemical Vapor Deposition," submitted to Appl. Phys. Lett.

Conference Presentations:

1. J. C. Chen, W. K. Chen, and Pao-Lo Liu, "Metalorganic Chemical Vapor Deposition of InSb Using Tri-Neopentyl Indium," Symposium on Innovative Science and Technology, Los Angeles, California, September, 1987.

2. J. C. Chen and P. L. Liu, "Epitaxial Growth of InSb on CdTe Substrate by MOCVD," Topical Conf. Compound Semiconductor Growth, Processing, and Devices, Gainsville, Florida, October, 1987.

Task 3

Laser Interaction and Deposition with Semiconductors

H.S. Kwok,
Electrical and Computer Engineering
State University of New York at Buffalo

M. Sheik-bahae, Ph.D. granted 1987,
Robert Barone, Ph.D. expected 1989,
Q.Y. Ying, Ph.D. expected 1990.

Technical Summary

During the duration of the grant, we were able to investigate the high laser intensity interaction behavior with semiconductors and metals. This result is important because of the need to understand surface phenomena which may be relevant to the deposition process. We found that tunneling ionization is important for the generation of carriers in low bandgap materials. This is a phenomena that has been ignored in the past.

In a separate experiment, we were able to measure the ion emission from a metal surface during laser irradiation. The most interesting result is that ions were observed at very low laser fluences (~ 40 mJ/cm^2), and that the laser frequency is below the normal work function of the material (aluminum). This result is totally unexpected and bears tremendous consequence to laser-target interaction behavior, either in laser deposition situation or in space weapon environment.

Two publications are enclosed in this final report.

TASK 4

Structural Studies of GaAs and Related Compounds Using X-Ray and Raman Techniques

C.R. Wie,
Electrical and Computer Engineering
State University of New York at Buffalo

Students : J.F. Chen, Ph.D. expected in Fall 1989 or Spring 1990,
H.M. Kim, Ph.D. expected Fall 1992.

Facilities improvements were made in the double crystal x-ray topography technique, liquid phase epitaxial growth system, and the Hall effect and photocurrent measurement system. The liquid phase epitaxial reactor is now being used to routinely grow various GaAs and InP layers. The double crystal topography technique has been completed and used to study strained-layer GaInAs on GaAs substrates grown by MOCVD (the preprint is attached).

Several micron thick GaInAs layers were grown on the buffer layers of Strained Layer Superlattice (SLS), graded GaInAs, or plain GaAs which had been grown on GaAs(001) substrates. The epitaxial GaInAs layer quality and the lattice relaxation were studied using Nomarski optical microscope, double crystal x-ray topography, and the x-ray rocking curve technique. The layers grown on a plain GaAs buffer or a graded GaInAs buffer layer showed surface line defects aligned along <110> directions. These surface cross-hatched patterns did not appear for the GaInAs layer grown on a SLS buffer layer [1]. All the GaInAs layers were relaxed by varying degrees. The lattice mismatches along the two <110> in-plane directions were different from each other, producing an additional unit cell distortion in addition to the tetragonal unit cell distortion which exists in all strained heterojunction layers [1].

Elastic strains in the MBE-grown strained GaInAs layers on GaAs substrates were measured using the rocking curve technique [2]. The elastic strains were correlated with the LO phonon frequency measured by the Raman technique. The strain-induced frequency shift was calculated and subtracted from the total measured phonon frequency, generating the bulk-equivalent phonon frequency as a function of composition for the GaInAs ternary layers. This is shown in Fig.1 of ref.[2]. The bulk-equivalent phonon frequencies for the GaInAs layers for all the composition range is reported in Fig.2 of ref.[3]. Knowing the bulk-equivalent phonon frequency for the ternary alloy allows one to use the Raman technique to measure the elastic strain. The elastic strain which can be measured reliably from the Raman measurements is 0.3% or higher which corresponds to 1 cm^{-1} frequency shift. For strains smaller than 0.3%, the double crystal x-ray rocking curve technique is the most reliable.

High energy heavy ion (15 MeV Cl) was used to bombard a GaAs substrate to a high dosage. Three different orientations (100), (110), and (111) were used to study the radiation defect-induced LO phonon shifts [4]. The beam-induced phonon frequency shifts were such that the TO mode shifts were essentially explained by the beam-induced lattice strain; however, the LO mode shifts of about 1 cm^{-1} were explained by the strain mechanism, leaving about 4 cm^{-1} unaccounted for [4]. This additional TO-LO splitting by the ion beam damage lead us to believe that the effective ionic charge of the ion beam-induced point defects is responsible for the phonon frequency shift in ion-bombarded semiconductor crystals. This proposed mechanism is different from the confinement model which uses the reduced mean free path

of phonons in an ion-damaged semiconductor crystals [5]. The phonon confinement model does not seem to explain the additional LO-TO splitting in the ion-damaged GaAs crystals.

References

1. C.R. Wie, H.M. Kim, and K-M Lau, SPIE Proc. Vol.877 (1988), in press (Preprint attached).

2. G. Burns, C.R. Wie, F.H. Dacol, G.D. Pettit, and J.M. Woodall, Appl. Phys. Lett. 51, 1919-1921 (1987). Reprint attached.

3. G. Burns, C.R. Wie, F.H. Dacol, G.D. Pettit, and J.M. Woodall, Matr. Res. Soc. Symp. Proc. Vol. 102 (1988), in press (Preprint attached).

4. G. Burns, F.H. Dacol, C.R. Wie, E. Burstein, and M. Cardona, Solid State Commun. 62, 449-454 (1987). Reprint attached.

5. P. Parayanthal and F. Pollak, Phys. Rev. Lett. 52, 1822 (1984).

Journal Publications

1. G. Burns, C.R. Wie, F.H. Dacol, G.D. Pettit, and J.M. Woodall, "Phonon shifts and strains in strain-layered (Ga,In)As", Appl. Phys. Lett. 51, 1919-1921 (1987)

2. G. Burns, F.H. Dacol, C.R. Wie, E. Burstein, and M. Cardona, "Phonon shifts in ion-bombarded GaAs: Raman measurements",Solid State Commun. 62, 449-454 (1987).

Conference Presentations

1. C.R. Wie, H.M. Kim, K.M. Lau, "Nondestructive characterization of MOCVD-grown GaInAs/GaAs using rocking curve and topography", to be published in Micro-optoelectronic materials ed. by Kukkonen, SPIE Proc. Vol. 877 (1988).

2. G. Burns, C.R. Wie, F.H. Dacol, G.D. Pettit, and J.M. Woodall, "Phonon shifts and strains in strain-layered (Ga,In)As", Matr. res. Soc. Symp. Proc. Vol. 102 (1988), in press.

TASK 5

Fabrication and Characterization of MS and MIS Structures on Si and InP

W.A. Anderson, Principal Investigator, Electrical and Computer Engineering.

K. Reinhardt, Research Assistant, M.S. Degree 5/88,
Now at Air Force Wright Aeronautical Lab.

B. Lee, Research Assistant, Ph.D. expected 1/90

A. Singh, Visiting Scholar

5.1 Low-Temperature Characterization of InP-MIS Devices

Indium phosphide (InP) is becoming of great interest because of its high carrier mobility, improved radiation resistance and ability to support oxide growth for surface passivation. Thus, InP holds great promise for high-speed, harsh environment and MOS applications. Our recent work on metal-insulator-semiconductor (MIS) structures using Zn-doped InP has also revealed utility as a temperature sensor.

After suitable cleaning procedures, ohmic contacts were formed on Zn-doped (100) InP using evaporated Zn/Au layers followed by annealing in forming gas. This was followed by thermal oxide growth in O_2 at 350° C with subsequent deposition of Au or Yb metals to form rectifying contacts. Oxide thickness was purposely varied from 10 Å to 90 Å to give a refractive index ranging from 1.6 to 2.2 which reflects different oxide phases. Current-voltage (I-V) data showed high quality rectification with a log I-V plot revealing linearity over 3-5 orders of magnitude and an ideality factor (n) ranging from 1.02 - 2.15 depending on oxide thickness. Ideality factor was temperature independent for Yb- contacts but increased with temperature for Au- contacts. Capacitance-voltage-temperature (C-V-T) data gave a 0° K barrier height ranging from 1.2 - 1.35 eV. As a temperature sensor, MIS diodes were subject to a constant current of 1.0 A and voltage measured as

a function of temperature from 80°K - 400°K. Thin oxide (10 Å for MS) gave dV/dT = 2.4 mV/°K whereas thick oxides (90 Å for MIS) gave dV/dT=3.0 mV/°K for both Au and Yb- contacts. These devices behaved consistently with repeated temperature cycling. Yb- sensors were linear from 100°K - 400°K whereas Au-ones became nonlinear for T<200°K. These differences can be explained from I-V-T data.

The InP temperature sensors described herein are of interest because of the linearity of Yb- devices from at least 100 K to 400 K and the sensitivity of 3.0 mV/°K which is greater than for Si-temperature sensors. These may later be integrated with III-V laser-detector chips for temperature compensation activities.

5-2 Hole and Electron Traps in Zn-Doped InP Using Ytterbium-Schottky Diodes

High barrier height Schottky diodes were prepared by the evaporation of Yb on Zn-doped, bulk grown p-InP. Prior to evaporation of Yb metal, a thin (20-35 A) oxide layer was terhmally grown. The diodes showed an ideality factor n=1.05, reverse saturation current density $J_o=3\times10^{-9}A/cm^2$, carrier concentration of $5\times10^{15}cm^{-3}$ and a barrier height of 1.02 eV. Deep level transient spectroscopy (DLTS) was done in the temperature range 90-450 K, for six rate windows between $20s^{-1}$ and 10^3s^{-1} with reverse bias (V_R), fill pulse height (V_p), and fill puse width (W), as parameters. At V_R=3V and V_p=0.6V, two hole traps ($E_{h1}=E_v+0.56$ eV, $\sigma_{h1}=3.4\times10^{-18}cm^2$, $N_{T1}=1\times10^{14}cm^{-3}$; $E_{h2}=E_V+0.12$ eV, $\sigma_{h2}=1.4\times10^{-17}cm^2$, $N_{T2}=5\times10^{12}cm^{-3}$) and one electron trap ($E_e=E_C-0.40$ eV, $\sigma_{e3}=8.7\times10^{-18}cm^2$, $N_{T3}=2.5\times10^{13}cm^{-3}$) were detected. $\sigma_{p1}=6.9\times10^{-18}cm^{-3}$ was separately determined using capture rate from the variation of the trap peak height with W which is close to the value obtained from thermal emission rate.

Variation of V_R between 3 V and 0.3 V indicated a linear dependence of the energy of the strongest hole trap level, E_{h1}, from E_V+0.56 eV at V_R=3V to E_V+0.34 eV at V_R=0.3 V. This indicates that the same hole trap does not extend over the entire space charge region. From the DLTS measurements at forward bias, V_F=0.2 V and V_p=0.6 V, the parameters of the hole traps near the interface were determined to be $E_h=E_V+0.24$ eV, $\sigma_h=2.8\times10^{-21}cm^2$, and $N^T=1.3\times10^{14}cm^{-3}$.

Thermally stimulated capacitance (TSCAP) studies involved a forward bias V_F=0.6 V, cooling to 90 K, bias switching to a reverse bias V_R=4.0 V and then heating at a constant rate to 450 K. The junction capacitance was recorded as a function of temperature for heating rates between 0.05 K/s and 0.5 K/s, and corrected for temperature dependence of diffusion voltage and the dielectric constant. This revealed three capacitance steps; one due to a strong hole trap level and two others for electron traps. The temperature dependence of the TSCAP data at a constant heating rate gave energy of the strong hole trap level at $E_{h1}=E_V+0.53$ eV whereas the electron trap levels were located at 0.36 eV and 0.24 eV below the conduction bandedge. Plots of dC/dT vs. T at different heating rates gave the activation energy, $E_{h1}=E_V+0.59$ eV and capture cross section $\sigma_{h1}=2.6\times10^{-21}cm^2$ of the hole trap. This information is useful when considering InP for electro-optic applications.

5.3 Oxide Integrity in Metal-Thin Oxide-Si Structures: E-Beam Effects in VLSI Applications

OBJECTIVE

Submicron and ultra-submicron structures require specialized

lithography techniques where electron-beam [EB] methods are playing a major role. The study reported herein concerns a comparison of thick (500 ^{o}A) to thin (190 ^{o}A) oxides on Si and the relative effects of a scanned electron beam on oxide integrity. The scanned electron beam is meant to simulate exposure required in electron resist. A study of MOS device performance, before and after E-beam exposure, represents the focus of this work. Properties utilized in the comparison include optical properties of the oxide, oxide trapped charge, interface state density and breakdown voltage.

EXPERIMENTAL TECHNIQUES

Wafers were chosen from a lot of (100), B-doped, 1 Ω-cm Si having one face polished to a mirror finish. Wafers were first de-greased in electronic-grade trichloroethylene (TCE), acetone and methanol. The native oxide was removed in buffered hydrofluoric acid followed by a thorough rinse in 18 MΩ deionized water. Oxide was grown using a special cycle for preserving carrier lifetime in the wafer. The cycle for 500 Å oxides consisted of: wafer insertion in a 600^{o}C furnace with 5 LPM N_2; ramp to 800^{o}C and hold 10 minutes in 5 LPM N_2+5 LPM O_2; ramp to 950^{o}C and hold 30 min; cool to 500^{o}C in 5 LPM N_2 and hold 30 min; slowly remove the wafers. Some oxides were grown with a Cl-content using a similar cycle except that for T>800^{o}C, O_2 was bubbled through electronic grade TCE using 8 LPM N_2 and 0.8 LPM O_2. Thin (<200 Å) oxides were grown similar to the thick ones except that only a 15 minute soak was used at 950^{o}C.

Following oxide growth, photoresist procedures were used to remove the oxide from the back of the wafer. Al was then evaporated to a thickness of 0.5-1.0 μm at a vacuum of $2x10^{-6}$ Torr. The Al contact was then sintered for a few seconds at 600^{o}C. Some samples were then ready for testing using a

mercury probe. Others were finished by evaporating a metal gate consisting of 100 ^{o}A Cr followed by 0.5-1.0 μm Al. An Hg-probe could also be placed beside an evaporated contact for purposes of comparison or used in place of an evaporated contact. Electron irradiation was accomplished utilizing a JEOL-T20 scanning electron microscope set at 20KeV and a beam current of 10^{-8}A. This resulted in a fluence of 0.6MRad (Si) or 3.8×10^{12} e/cm^2 or 6×10^{-7}C/cm^2.

EXPERIMENTAL DATA

Thick Oxides

Ellipsometry studies on standard oxides, modelled as a uniform film, indicate a decreasing refractive index, from 2.10 for a 7 Å oxide to 1.60 for a 75Å one to 1.46 for a 600 ^{o}A one, showing the influence of the transition region (δ) from Si to SiO_2. Cl-oxides had an increased breakdown field (E_{BD}) whereas pre-irradiated oxides had a significantly reduced E_{BD}. E-beam exposure reduced E_{BD} with the Cl-oxide still exhibiting a higher value.

The shift in the experimental high frequency C-V curves along the voltage-axis indicates the existence of oxide charge. The Cl-oxide exhibited 2.4×10^{-7}C. whereas that in the pre-irradiated oxide, 1.1×10^{-7}C., is the same as for the standard. Cl in the oxide most likely introduces positive charged Cl^+ states in addition to those normally present. After e-beam exposure, the horizontal shift indicates oxide charge, with the Cl-oxide having an increased charge of 1.3×10^{-7}C. compared to 0.6×10^{-7}C. for the standard.

The low frequency (LF) C-V data initially show a small "hump" at about

-0.5 V indicating an interface perturbation at that point. An upward shift in LF data after e-beam exposure for the standard oxide indicates an increased interface state density from $3x10^{11}/cm^2$-eV at mid-gap to $12x10^{11}/cm^2$-eV. The difference in experimental LF C-V data compared to the ideal indicates the Cl-oxide to give the lowest surface state density (D_{it}) at mid-gap but not towards the band-edge. After e-beam scan, the Cl-rich samples increase in D_{it} from $5x10^{10}/cm^2$-eV to $5x10^{11}/cm^2$-eV near mid-gap. The sample irradiated prior to contact formation behaves similarly to the standard one irradiated after contact formation.

Thin Oxides

Refractive index values are slightly higher than for thick oxides which may reflect the greater influence of the transition region, δ. Average breakdown field prior to and after e-beam scan is greater than that of the thick oxides. High frequency C-V data are slightly shifted to the left from the standard for data taken prior to and after e-beam scan. The small magnitude shift indicates a small oxide charge of about $1x10^{-10}$C. with no significant change after e-beam scan. Prior to e-beam scan, the LF-C-V data are quite close to ideal indicating a small surface state contribution. After the e-beam scan, there is a slight upward shift indicating a slightly increased surface state contribution from $2\text{-}4x10^{11}/cm^2$-eV at mid-gap and a greater change near the band-edge.

5.4 Publications and Conferences

1. K.D. Reinhardt, A. Singh and W.A. Anderson, "Ytterbium Metal-Insulator-Semiconductor Contacts to InP", Solid State Electronics, in press.

2. W.A. Anderson, C.L. Au and Y.S. Lee, "Electron Beam Damage in MOS Structures with Ultra-Thin Oxides", Workshop on Process-Related Electrically Active Defects in Semiconductor-Insulator Systems, Research

Triangle Park, Sept. 1-2, 1987.

3. C. Warren, K. Reinhardt, A. Singh and W.A. Anderson, "Effects of Surface and Bulk Defects in InP", Proc. Matls. Res. Soc. Fall Mtg., Boston, Nov. 30 - Dec. 5, 1987.

4. W.A. Anderson, A. Singh, K. Jiao and B. Lee, "Deep Levels and Radiation Effects in p-InP", Space Photovoltaic Research and Technology Conference, NASA-Lewis in cleveland, Apr. 19-21, 1988.

5. K.C. Reinhardt, M.S. Thesis, "Study of InP Metal-Semiconductor and Thin Insulator Metal-Insulator-Semiconductor Diodes", May, 1988.

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Appendices

Reprints of Publications and Conferences

(Copies sent only to Nelson and Davis)

Ion Emission During Low Fluence KrF Laser-Metal Interaction

Two-Photon and Three-Photon Absorption Coefficients of InSb

Metalorganic Chemical Vapor Deposition of InSb Using Tri-neopentylindium

Low Temperature Heteroepitaxial Growth of InSb on CdTe

Nondestructive Characterization of MOCVD-Grown GaInAs/GaAs Using Rocking Curve and Topography

Phonon Shifts and Strains in Strain-Layered $(Ga_{1-x}In_x)As$

Phonon Shifts and Strains in Strain-Layered $(Ga_{1-x}In_x)As$

Phonon Shifts in Ion Bombarded GaAs: Raman Measurements

Effects of Surface and Bulk Defects in InP

Deep Level and Radiation Effects in p-InP

Ytterbium Metal-Insulator-Semiconductor Contacts to InP

Oxide Integrity in Metal-Thin Oxide-Si Structures: E-Beam Effects in VLSI Applications